Structure and Phason Energetics of AlCo Decagonal Phases

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Abstract

We develop a model for AlCo decagonal quasicrystals and approximants. Our model defines a large number of potential atomic positions. These sites are populated by two atomic species that interact with each other through electronic-structure-based pair potentials. Monte Carlo simulation of the model produces realistic atomic configurations for AlCo alloys at the temperature and composition range where a metastable decagonal quasicrystal exists. The resulting structures generally consist of packings of space by pentagonal bipyramid (PB) clusters. Projections of the centers of these clusters form tilings of hexagons, boats and stars. We identify atomic displacements associated with phason fluctuations. We note a distinction between "simple" phason *hops* involving predominantly Al atom motion and "collective" phason *flips* that transport the Co atoms.

I. INTRODUCTION

A fundamental question in the science of quasicrystals is "where are the atoms?"(Bak 1986a). Experiments provide partial answers, but often cannot resolve the precise position or chemical identity of a small subset of the atoms. Theory can assist experiment. As in ordinary crystallography (Stout and Jensen 1989), total energies for plausible configurations consistent with experimental data can be calculated, and the more favorable structures identified. In addition to improving our knowledge of where the atoms are, we receive a bonus of understanding *why* they choose particular positions. Further, we can identify important structural changes and associated energetics. A topic of lively debate in quasicrystal science is the distinction between entropic and energetic stabilization of the quasicrystalline state (Widom 1990, Henley 1991, Ingersent 1991, Socolar 1991). Accurate structural models and total energy calculations can help resolve this debate. The modeling presented in this paper is unbiased with regard to the mechanism of quasicrystal stabilization.

Early theories of quasicrystals focused on tilings of space without explicit reference to the relationship between individual tiles and real atoms. Cluster models propose reasonable local atomic structures, but may leave a small amount of empty space around the clusters, or else suffer from unreasonably short interatomic distances. Similar difficulties plague "atomic surface" (Bak 1986b) descriptions of quasicrystal structure. These difficulties led to a proliferation of nearly identical proposed structures differing from one another mainly in the placement or chemical identity of a small number of atoms. We feel it is important to systematically compare possible structures with each other, discriminating on the basis of total energy (Cockayne et al. 1993; Phillips and Widom 1993) for zero temperature stability, and free energy at finite temperatures.

Recently, *ab initio* electronic structure calculations have been used in the case of AlPdMn to find the most stable large decagonal approximants (Krajčí, Hafner and Mihalkovič 1997). To investigate structures as complex as quasicrystals and their approximants at thermal equilibrium, however, it is necessary to be able to rapidly evaluate energies for large number of configurations. First-principles methods are not practical at present; therefore, effective interatomic potentials are required.

All known *stable* quasicrystals (i-AlCuFe (Tsai, Inoue and Masumoto 1987), d-AlCuCo (d-AlNiCo) (Tsai, Inoue and Masumoto 1989), i-AlPdMn (Tsai et al. 1990), etc.) are at least ternary compounds. To date, no effective interatomic potentials are known for any stable quasicrystal forming systems, so attention must be focused on binary alloys. Electronic-structure-based pair potentials exist for binary alloys of aluminum with cobalt (Phillips et al. 1994) and manganese (Zou and Carlsson 1993a, 1993b). The binary AlCo alloy is a good system to study via pair potentials, because it contains a metastable quasicrystalline phase. Related stable crystal phases possess local structures with five-fold symmetry. Al and Co are also constituents of stable decagonal AlCuCo and AlNiCo. This paper describes in detail our investigation of AlCo alloys related to decagonal quasicrystals (Widom and Cockayne 1995, 1996).

Several stable and metastable complex phases occupy a small composition interval in the binary $Al_{1-x}Co_x$ system for $0.23 \leq x \leq 0.29$ (Grushko et al. 1995). Most of these phases, including a decagonal phase (d-AlCo), share an 8 Å stacking periodicity in the z-direction, and possess similar structural units separated in the plane by 6.5 Å . These structural units form tilings of hexagons in the solved structures of monoclinic $Al_{13}Co_4$ (Hudd and Taylor 1962) and orthorhombic Al_3Co (Grin et al. 1994, Li, Ma and Kuo 1994, Widom et al. 1995), and appear to form tilings of hexagons, boats (crowns) and stars in HREM images of larger approximant phases (Ma and Kuo 1995b). We will sometimes refer to this family of related structures under the name "Al_3Co". The fact that tiles shaped like hexagons, boats and stars comprise the Al_3Co structures suggests that the same tiles also comprise the decagonal phase. We call this model the "hexagon-boat-star (HBS) tiling model" (Li 1995) for d-AlCo. The simplest quasiperiodic HBS tiling is given by a subset of the vertices of the two dimensional Penrose tiling and is an example of a "two-level tiling" (Tang and Jarič 1990, Li and Kuo 1991, Henley 1991, Henley 1993) (Figure 1(a)). Many other HBS tilings are also possible (Figure 1(b)). A slight variation on the HBS tiling model, where a fourth tile shaped like a decagon is allowed (Li 1995), seems to describe decagonal phases such as AlPdMn (Li and Dubois 1994). We call this the "HBSD" model.

The solved low temperature Al_3Co structures alternate flat (F) and puckered (P) layers of atoms separated by approximately 2 Å, and have a periodicity of 4 layers in the z direction.

The stacking sequence is $FPF'P'$, where F' is a variant of F, and P' is P mirrored in a horizontal plane. The only known exception, $Al_{11}Co_4$ (Li et al. 1995), is stable only at high temperatures. It alternates layers similar to the F and P types with a net 4 Å periodicity, and is closely related to the 8 Å structures. Structural units separated horizontally by 6.5 Å consist of $Al_{16}Co_7$ pentagonal bipyramids (PB's) (Figure 2). The equator of the PB features a pentagon of Co atoms in a flat layer with edge length 4.7 Å centered by an Al atom. Co atoms in adjacent puckered layers lie on the (pseudo) pentagonal axis of the PB and are forced away from this central Al, causing the puckering of those layers. The PB occupies 3 layers along the stacking axis. Two PB's separated by $c = 8$ Å along z are joined by a 4th "junction" layer consisting of a highly distorted pentagon of Al (including frequent vacancies) in a flat layer. Flat layers F and F' differ by interchanging PB equators with PB junctions. Figure 3 shows the recently solved structure (Grin et al. 1994) of orthorhombic Al_3Co. PB equators and flat layer junctions are visible in Figure 3(a), while the PB caps fill Figure 3(b).

Because two flat layers occur per 8 Å along the stacking axis, there are two choices of level on which to center the PB. When centered on the flat layer F we call label the PB "+". The Co in layer P, just above F, is displaced upward to accommodate the centering Al. When centered on the flat layer F' we label the PB "–". The Co in P just below F' is then displaced downward. Vertical displacement of Co atoms in puckered layers relates to the centering of PB's in layers F or F'. Because our description is Ising-like (i.e. a Z_2 symmetry), we use the Ising spins to describe the centering of the PB's or the "puckering pattern". Figure 4 shows the puckering patterns observed in monoclinic $Al_{13}Co_4$ and orthorhombic Al_3Co.

Combining the HBS tiling model with the PB structure described above suggests that the 8 Å decagonal phase consists of PB's on the vertices of a HBS tiling. We call this model the "PB/HBS tiling model" for 8 Å decagonal phases. The model "PB8" proposed by Henley (1993) was a PB/HBS tiling model. Significant structural rearrangements are easily described within the context of the PB/HBS tiling model. A transformation, which effectively shifts the centers of the PB's in a single column by 4 Å along the column, changes the sign of the PB. We call this transformation a “puckering flip”. A second transformation is the minimal transformation that changes one HBS tiling into another. We call this transformation a “phason flip”. An alternate name for this transformation would be “tiling flip”, and we use the two names synonymously. In a phason flip, the PB’s in one column effectively shift by 2.5 Å and rotate 180 degrees.

In this paper, we explore the thermodynamics, equilibrium structures, and energetics of 8 Å periodicity AlCo alloys with finite temperature Monte Carlo. Among our results:

• Favored atomic configurations are well described within the PB/HBS model.

• The average structure of a 508-atom approximant is found and presented as atomic surface maps. Cobalt atoms mainly occupy atomic surface interiors.

• Phason disorder similar to partial occupancy in quasicrystal approximants (Hudd and Taylor 1962, Mahne and Steurer 1996) is prevalent at Al sites near atomic surface edges.

• Individual atomic phason hops (Frenkel, Henley and Siggia 1986) and collective atomic motions resulting in puckering flips or phason flips turn out to cost little energy.

The following section presents model atomic surfaces chosen to be consistent with known AlCo crystalline approximant phases, and to generalize those structures to the quasicrystal. Section III explains our Monte Carlo simulation method and the pair potentials used for total energy calculations. Section IV describes our main results on structure (IV.A) and energetics (IV.B). Finally, Section V summarizes our key results, and discusses improved methods for future studies.

II. ATOMIC SURFACES

Quasicrystalline structures can be succinctly described in terms of atomic surfaces (Bak 1986b). Although the shapes of atomic surfaces for a quasicrystal are not necessarily *simple* (Gähler 1988, Cockayne 1995), diffraction experiments on decagonal quasicrystals (Steurer and Kuo 1990, Steurer 1991, Steurer et al. 1993, Steurer et al. 1994) show that the vast majority of atoms belong to a set of distinct atomic surfaces, and that these atomic surfaces are relatively flat. They are strongly localized in "parallel space" while being quite extended in "perpendicular space". Since the precise shapes of the atomic surfaces for the d-AlCo structure are unknown, we include in this work all the sites that belong to a set of oversized atomic surfaces. The number of sites included is therefore much greater than the number of atoms. Atomic surface sizes and shapes are deliberately chosen to include any likely low-energy structure as well as the dominant fluctuations about these structures.

In the following we use the cut method, beginning with a five-dimensional (5D) lattice. The three-dimensional physical (parallel) and two-dimensional perpendicular space components of the 5D basis vectors used here are:

$$\mathbf{e}_i = [(\mathbf{e}_i^{\|}), (\mathbf{e}_i^{\perp})] \equiv \begin{cases} [a_0(\cos(2\pi i/5), \sin(2\pi i/5), 0), a_0(\cos(6\pi i/5), \sin(6\pi i/5))], & i < 5; \\ (0, 0, c, 0, 0), & i = 5, \end{cases} \tag{2.1}$$

where a_0 (the quasi-lattice constant) and c are lattice parameters to be determined by experiment. We use $a_0 = 1.529$ Å and $c = 8.120$ Å for our calculations. Most atomic surfaces are centered on 5D sites of the form (n_1, n_2, n_3, n_4, z); *i.e.* the first four coordinates are integer. In this case, we define the level ν of the atomic surface to be

$$\nu = (\sum_{j=1}^{4} n_j) \bmod 5. \tag{2.2}$$

Since the atomic surfaces are distinguished by coordinate ν, the actual periodicity of the 5D structure is the superlattice of the lattice generated by Eq. 2.1 which leaves ν invariant. An atom in the quasicrystal located at position $\mathbf{r}$ has $(\mathbf{r}^{\|}, \mathbf{r}^{\perp}) = (\mathbf{r}, 0)$ and is associated with a nearby "ideal site"

$$(\mathbf{r}, 0) = (\mathbf{r}_{ideal}, 0) + (\Delta\mathbf{r}^{\|}, 0); \tag{2.3}$$

$$(\mathbf{r}_{ideal}, 0) = \sum_{j=1}^{4} n_j(\mathbf{e}_j^{\|}, \mathbf{e}_j^{\perp}) + z(\mathbf{e}_5^{\|}, \mathbf{e}_5^{\perp}) + (0, \Delta\mathbf{r}^{\perp}). \tag{2.4}$$

For an approximant, Eqs. 2.3-2.4 still hold, except that the form of the $\mathbf{e}_i^{\perp}$ in Eq. 2.1 must be altered appropriately (Edagawa et al. 1991, Fettweis et al. 1994).

For a given atom, the decomposition into $\{n_j\}$ is not unique, but in the solved Al_3Co approximants, nearly all the atoms have a unique solution to Eq. 2.3-2.4 such that $|\Delta\mathbf{r}^{\|}| < 0.4$ Å and $|\Delta \mathbf{r}^{\perp}| < a_0$. For such atoms, we call $\mathbf{r}_{ideal}$ the *ideal site* for the atom. Inserting the corresponding values for n_j in Eq. 2.4 into Eq. 2.2, we find the value of ν associated with the ideal site and with the atom itself. Two atoms whose ideal sites are separated by τa_0 = 2.5 Å (a typical atomic near-neighbor distance), differ in ν by 2 (modulo 5). Centers of pentagonal bipyramids (PB), ideally separated by $\tau^3 a_0$ = 6.5 Å , also differ in ν by 2 (modulo 5).

From structures of solved approximants, we find appropriate atomic surface locations. We set the ideal sites for PB centers at levels 1 and 4, in agreement with the notation of Steurer et al. (1990,1993). Most remaining atoms in the flat layers occupy levels 0, 2 and 3. The puckered layers are simpler: nearly all the sites occupy levels 1 and 4 (see Figure 3). Although the z coordinates of the puckered layer atoms take a range of values, we make the simplifying approximation that all such atoms, except for certain "unpuckered" atoms described in the following paragraph, are located at exactly $(0, c/2) \pm p$, where p is a "puckering parameter" for AlCo. From the solved $Al_{13}Co_4$ structure, we averaged the z coordinates for the puckered layer atoms appropriately to obtain $p \approx 0.26$ Å . For convenience, we compiled a list of useful intersite distances in Table I.

Three types of atomic site that occur in the orthorhombic Al_3Co approximant are difficult to represent in terms of flat atomic surfaces. Using the notation of Grin et al. (1994), these are sites of type Al(7&26), Al(8) and Al(18) (see Figure 3). The latter two lie at sites of approximate inversion symmetry: Al(8) in the flat layer at the midpoint between two edge-sharing PB's; Al(18) in the puckered layer where two empty pentagons of Al meet tip-to-tip at the center of a long hexagon of PB's. In each of these two cases, ideal sites with integer coordinates lie symmetrically placed nearby. For the Al(8) sites, atomic surface 2 and 3 sites lie 0.76 Å away. For the Al(18) sites, atomic surface 1 and 4 sites lie 0.54 Å away, 0.47 Å in-plane and 0.26 Å vertically. The vertical puckerings occur in opposite directions so the averaged site is "unpuckered", as is nearly the case experimentally. We define the appropriate averages of the nearby ideal sites as extra "special" sites, shown in Figure 3.

The remaining difficult sites, the Al(7)-Al(26) pair, lie in the flat layer near the midpoint of a PB edge shared by two clusters and are asymmetrically displaced, respectively, 1.34 Å and 0.90 Å toward the centers of the two clusters (Grin et al. 1994). A pair of atomic surface 2 and 3 sites exist in similar positions, but with smaller and symmetric 0.76 Å displacements from the edge (see Figure 3). The Al(7) and Al(26) sites lie, respectively, 0.58 Å and 0.14 Å away from from these ideal sites. We rely on the existing ideal sites to approximate the Al(7 & 26) class of sites. The ideal sites are 1.53 Å apart while the experimental sites are 2.24 Å apart. In either case, the sites are so close together that it would be very costly energetically for both sites to be simultaneously be occupied by Al.

In all cases except the Al(7)-Al(26) pair, the displacement of experimental sites from ideal is less than 0.38 Å. To visualize the coincidence between ideal and experimental positions, consider spheres of radius 0.38 Å placed around every ideal site. Only 5% of the total volume of space would be filled, but 99% of the experimental sites would be covered by these spheres. The median deviation of experimentally measured sites from the nearest ideal site is 0.12 Å, a distance smaller than typical displacements due to thermal phonons at room temperature.

We extend the above analysis to find reasonable atomic surface shapes and sizes for larger approximants and the decagonal phase. We exploit the fact that the atomic arrangements observed in the AlCo approximants are locally two or three level packings and the fact that there is a very convenient limit to the range of atomic surface shapes for a good two/three-level packing: the atomic surfaces for levels ν, $\nu+2$ and $\nu-2$ lie within decagons of radius a, a and $\tau^{-2}a$, respectively (Olamy and Kléman 1989, Niizeki 1994). The AlCo approximants show that levels 0, 2 and 3 dominate in certain regions of the flat planes (see Figure 3). These atomic surfaces are set to be decagons of radius a, while the atomic surfaces for levels 1 and 4 are set to radius $\tau^{-2}a$. In the puckered layers, the occupied sites in the solved structures are exclusively level 1 and level 4 sites (or their averages as described above). We choose decagons of radius a for levels 1 and 4. We also include atomic surfaces of radius $\tau^{-2}a$ at levels 2 and 3 to allow for the possibility of three level packings in these layers.

The difficulty extrapolating from approximants to the quasicrystal is that the quasicrystal itself may contain sites cut from atomic surfaces so small that they are not contained in small approximants. For example, a boat and two hexagons could combine to form a 20 Å diameter decagon, reducing the number of vertices, as shown in Figure 5. The interior of an asymmetric 20 Å decagon in an PB/HBS tiling could undergo reconstruction to a decagonally symmetric arrangement (Beeli and Horiuchi 1994), turning it into a PB/HBSD tiling. The solved AlCo approximants are too small to contain the motifs shown in Figure 5 and hence cannot distinguish between an HBS tiling quasicrystal and an HBSD tiling quasicrystal. The centers of reconstructed decagons would be level 0 points and could naturally accommodate a (distorted) pentagonal bipyramid. For maximal local symmetry, these bipyramids would be centered at *unpuckered* positions in the puckered layer and the "pole" atoms would then be *puckered* positions in the flat layer. These potential sites are associated with the small atomic surfaces of radius $\tau^{-3}a$ included in Table II. We thus allow for the possibility of HBSD tilings in our system. Note how the distinction between HBS and HBSD tilings depends on very small atomic surfaces, that is, a very small fraction of the atoms.

With the atomic surface radii described above, the site list allows for a variety of quasiperiodic and approximant structures. Certain phason fluctuations cannot be represented, however, because the final atomic position would be outside this set. To model these fluctuations, which we expect to be important, we make the atomic surfaces oversized. We keep their decagonal shapes, but expand each radius by $\epsilon \equiv \tau^{-3}a/2 \approx 0.12\,a$. The value of ϵ was chosen to allow for what we estimate to be the important fluctuations while keeping the number of sites from being too large. In a two-dimensional maximally random random-tiling quasicrystal, for large approximants, ϵ should increase logarithmically (Widom, Deng and Henley 1989, Strandburg, Tang and Jarič 1989) as the size of the approximant. For three-dimensional icosahedral quasicrystals it should saturate (Tang 1990). The appropriate behavior for three-dimensional decagonal quasicrystals with equilibrium stacking disorder is still open to investigation (Henley 1991, Burkov 1991a, Shin and Strandburg 1993, Jeong and Steinhardt 1993).

After the atomic surfaces are oversized, we add the special sites with half-integer coordinates. All flat layer positions midway between level 1 and level 4 flat layer sites separated by 6.5 Å are added to the list, in order to include sites equivalent to Al(8) in Al_3Co. Additionally, sites at $z = \{0, 0.5\}$ which project to the center of a 6.5 Å by 7.6 Å rectangle of level 1 and 4 flat layer sites are included, in order to include sites equivalent to Al(18) in Al_3Co(see Figure 3).

Finally, all atomic surfaces are repeated at the additional values of z equal to $-z$, $0.5+z$ and $0.5-z$. Addition of the $-z$ sites allows the atoms in the puckered layers to shift to either of two puckering positions 0.26 Å above or below the middle of their layer. As a consequence, the periodicity of the list of sites is only 4 Å. However, we note that most models for 4 Å periodic decagonal quasicrystals (Yamamoto et al. 1990, Steurer and Kuo 1990, Burkov 1991b, Hiraga, Lincoln and Sun 1991, Steurer et al. 1993, Cockayne and Widom 1996) are incompatible with our atomic surfaces because we impose FP alternation (P10/mmm symmetry), while the 4 Å models alternate equivalent layers ($P10_5$/mmc symmetry), as implied by diffraction studies (Steurer and Kuo 1990).

III. MONTE CARLO APPROACH

We employ Monte Carlo simulation to assign atoms to sites. Over long runs, the simulation generates many possible atomic arrangements, each with a probability proportional to its Boltzmann weight. Our simulation uses the Metropolis method, generating a new configuration based upon the present atomic positions, and moving to the new configuration with a probability related to the change in total energy between configurations while obeying the requirement of detailed balance (Metropolis et al. 1953).

New configurations are generated by one of three moves. We permit a "small hop" of an atom to a neighboring site less than 2.5 Å away. We also permit "long hops" to any other site regardless of how far removed. Finally, we include "species swaps" in which an arbitrarily chosen Al-Co pair exchange positions. In steady state, the rate of transitions into a configuration must match the rate of transitions out of the configuration. Detailed balance guarantees that the steady state probability to be in some configuration is proportional to the Boltzmann factor $\exp(-E/k_BT)$ for the configuration.

Long hops and species swaps easily obey detailed balance using the ordinary Boltzmann factor to accept or reject the move. The small hops are more complicated, however, because some sites have more neighbors than other sites. Consider a small hop from site i to site j leaving all other atoms fixed. Let P_i and P_j be the Boltzmann factors for the initial and final configurations, respectively, and E_i and E_j the energies. The rate to go from i to j is

$$R_{i\to j} = \begin{cases} P_i\,\omega_i\,f_{ij}\,e^{-(E_j-E_i)/k_BT} & \text{if } E_j > E_i \\ P_i\,\omega_i\,f_{ij} & \text{otherwise} \end{cases} \tag{3.1}$$

where ω_i is the rate at which we attempt moves out of site i when it is occupied and f_{ij} is the fraction of attempted moves out of site i that go to site j. Let Z_i be the number of sites within the small hop size of site i, so that $f_{ij} = 1/Z_i$. Detailed balance requires equality of rates $R_{i\to j} = R_{j\to i}$, or

$$\frac{\omega_j Z_i}{\omega_i Z_j} = \frac{P_i}{P_j} e^{-(E_j-E_i)/k_BT}. \tag{3.2}$$

Inspecting Eq. (3.2) we note the right hand side equals unity in thermal equilibrium. In order for our simulation to produce this equilibrium distribution we must choose the rate ω_i of attempted transitions out of each site i in proportion to the number Z_i of sites within the small hop length of the site i.

Provided the list of possible sites is not too large, one may speed the simulation by pre-calculating atomic interaction energies. First form an array recording values of the interaction energy (including images under periodic boundary conditions) between an atom of type α at site i and an atom of type β at site j for all pairs of sites i and j and species α and β. Then, to calculate the potential energy of a given atom at site i just sum the values of this array over each occupied site j. The savings in simulation time is considerable, with a single evaluation of potential energy for our 508 atom system going about 50 times faster than is possible without using precalculated values. The disadvantage to this approach is the need to store large arrays in active memory.

Simulation efficiency is important because we need to reach from 10^5 to 10^6 Monte Carlo steps per atom. Such long runs are needed because of two peculiarities of our calculation. (1) Acceptance rates are low, typically .0026 for small atomic hops at T=1000K, so we must attempt large numbers of moves significantly change the configuration. (2) Average energy differences between configurations are small compared with random thermal fluctuations.

Quasicrystals possess a mode of elastic deformation, known as a phason mode, not found in ordinary crystals. One can conveniently distinguish phason modes from ordinary elastic phonon modes by representing the quasicrystal as a superposition of incommensurate density waves (Lubensky 1988), each with its own phase. Varying the relative phases of the waves with respect to each other creates zero energy "Goldstone Modes" of the quasicrystal. Certain combinations of phase changes (those that transform as vectors under rotation (Lubensky 1988)) generate continuous translations of the structure and correspond, at finite wavelength, to phonon modes. The orthogonal subspace of phase changes generates phason modes. Whereas phonon modes impart continuous atomic displacements to each atom, phason modes are believed to create discrete atomic hops (Frenkel, Henley and Siggia 1986) between nearby ideal sites. It is common to refer to such localized atomic hops as phasons, without regard to spatial correlations among hopping atoms. In the atomic surface description of a quasicrystal, an atoms on a sites near the edge of an atomic surface can hop to a nearly equivalent site near a different atomic surface edge. Because the two sites are nearly equivalent, the energy difference may be vanishingly small.

Our modeling technique places atoms only at ideal sites generally located at least 0.5 Å apart. Since the expected thermal phonon displacements of about 0.3 Å at T=1000K are insufficient to displace atoms from one ideal site to its neighbor, phonons are frozen out in our model. Thus, except for some purely vertical hops that relate to puckering flips, the atomic hops in our simulation are properly described as phason fluctuations. However, we simulate finite unit cell structures with periodic boundary conditions. These are ordinary (though complex) crystals and should not have phasons as long wavelength elastic modes. For these crystal structures, the phason hops correspond to a type of internal disorder in which many sites possess fractional occupancy.

Our Monte Carlo method loses the temporal information produced by molecular dynamics, but it retains the thermodynamic equilibrium state. Configurations are sampled with the proper frequency, they just appear in unusual order. In fact, the evolution pathways in Monte Carlo can be chosen at our convenience. By explicitly testing discrete atomic hops, atoms may move easily between nearby potential wells without the need to climb the barrier that separates them. Another move unique to Monte Carlo swaps atoms of differing chemical species. In reality this might require the participation of a nearby vacancy or a lattice dilation to give the atoms enough room to move in. Our simulation accomplishes the same task without these complications. We even allow hops and swaps of arbitrarily large distance, further reducing the time necessary for the simulation to equilibrate.

For atomic interactions we use pair potentials previously described in Phillips et al. (1994). These pair potentials represent the dominant term in the structural component of cohesive energy. They are derived by calculating the perturbation to an otherwise uniform free electron density caused by inserting a positively charged ion, then calculating the energy to place a second ion in the spatially varying density electron gas. The resultant Friedel oscillations in the potentials favor particular interatomic separations consistent with quasicrystalline structures (Widom and Cockayne 1996). Direct d-d interactions between transition metal atoms are not included. These may be expected to play a role when transition metal atoms lie close together (less than about 2.5 Å), but in the actual structures the transition metal atoms lie 2.9 Å or more apart. The full cohesive energy should include three body and higher order interactions. Fortunately, the two-body term alone seems to reproduce adequately the experimentally determined phase diagram in the composition regime of interest up to about 27% Co (Phillips et al. 1994).

The pair potentials include a smooth cutoff beyond 10 Å . We employed periodic boundary conditions in our simulations. Typically the simulation cell was just a single unit cell length along the a and b axes, but was doubled to achieve a length of 16.24 Å along the c axis. Thus no atom interacted strongly with periodic images of itself.

IV. RESULTS

Using the simulation method outlined in Section III, we acquire data relevant to two important problems: structure and energetics. Most configurations produced in the simulations can be described in terms of cluster packings, allowing us to describe an ideal alloy structure both in real space and in terms of atomic surfaces. By comparing total energies of different configurations we calculate energies of single- and multi-atom displacements. We identify changes in structure and energy related to phason hops and to puckering and tiling flips.

A. Structure

We investigated several orthorhombic approximants in the h/k series (Edagawa et al. 1991, Fettweis et al. 1994). A remarkable number of approximants to different decagonal phases belong to this family (Liao et al. 1992). Even the $Al_{13}Co_4$ monoclinic phase can be looked at as a slightly distorted supercell of a 3/2 orthorhombic approximant (see Figure 4). Simulations on periodic approximants allow the atomic structure of small approximants to be compared with known results and the atomic structure of large unsolved approximants to be predicted. The results on the approximants can then be extrapolated to a plausible model for the decagonal quasicrystal phase.

Before any simulation can begin we must decide on an appropriate atomic density and chemical composition. We use a known structure as a guide. The $Al_{13}Co_4$ monoclinic phase (Hudd and Taylor 1962) has 102 sites per unit cell, occupied by 72.8 Al and 24 Co. Assuming that all Co atoms for any h/k approximant belong to PB's and that the PB's lie on an HBS tiling, there are 8 F_{h+k-1} Co per cell, F_i being the ith Fibonacci number (we choose the origin of the Fibonacci Series $F_1 = F_2 = 1$). The "proper" number of Al atoms for the other approximants should be near the closest integer to $72.8\,\tau^{h+k-5}$. This suggests the decagonal phase lies at about $\lim_{n\to\infty}(8F_n)/(8F_n + 72.8\,\tau^{n-4}) \approx 25.2\%$ Co, and the approximant phases should converge towards this value. Fortunately, the corresponding electron density is 0.1808 per Å^3, almost exactly the same as the density in pure Al for which the pair potentials were calculated.

The ideal lattice parameters a and b for an h/k approximant are $a = \sqrt{5}\tau^{h+1}a_0$ and $b = 2\cos(\pi/10)\tau^k a_0$. We focus our attention on three particular approximants: the 2/3 approximant, with lattice constants $a = 14.48$ Å and $b = 12.32$ Å, with composition $Al_{73}Co_{24}$; the 3/2 approximant with lattice constants $a = 23.43$ Å and $b = 7.61$ Å, with the identical composition; and especially the 3/4 approximant with lattice constants $a = 23.43$ Å and $b = 19.93$ Å and composition $Al_{190}Co_{64}$. The 3/4 approximant has not been observed in AlCo, but it provides a bridge between the solved 2/3 Al_3Co approximant and the larger AlCo approximants reported (Ma and Kuo 1992, Ma, Li and Kuo 1995a, Ma and Kuo 1995b), as well as the metastable decagonal phase itself.

The simulation described in Section 3 was performed on all three approximants to test the PB/HBS tiling model. Long runs were performed on each approximant and configurations separated by long time intervals were examined from each simulation. A systematic way of associating a PB/HBS tiling with a configuration is needed. Our results suggest that examination of the Co atoms *alone* is sufficient to identify PB's and the puckering pattern. The characteristic of a PB is a Co pentagon in the equator and junction layers with the Co atoms in the puckered layers on pole positions displaced away from the PB equator. We examined the Co positions in each sample configuration to determine the location of PB's. All independent coordinates (x, y) in the site list were considered as possible PB axes. Two PB's, each containing 5 equator Co and 2 pole Co's, as well as 2 junction layers each containing 5 junction Co's can be accommodated by the (doubled) c =16 Å periodicity, for a total of 24 Co's per ideal vertically stacked PB's. For each configuration tested, the number of Co atoms matching Co positions for the ideal PB's was counted for each possible cluster center, and then the centers were ranked in order of agreement with the ideal PB.

Suppose that the simulation of a 3/4 approximant yielded a perfect PB/HBS tiling. There would be a 24 atom (or 100%) coincidence between ideal and actual Co positions for each of the 10 PB axes. Additionally, there would be axes external to the actual PB axes with a large coincidence between actual and ideal Co positions. Detailed consideration of the geometry of each possible tiling (Figure 6) shows that the maximum coincidence for an external axis is 16 Co atoms (2/3 of the maximum 24) and that there are several such axes for each tiling. Now suppose, on the other hand, that the simulation structure were completely random. Then the ranked Co coincidence count would be a smoothly decreasing function of rank. The intermediate case of a PB/HBS tiling with slight Co disorder would yield 10 axes with near perfect agreement and several with close to 2/3 agreement.

The results for our simulation are shown in Figure 7, where we plot the average Co coincidence fraction versus rank for the 3/4 approximant simulation. The signature of a PB/HBS tiling with only slight Co disorder is evident. First, the coincidence fraction for ranks 1-10 is close to unity showing that ten 10 PB axes can be identified per configuration. Second, the coincidence fraction jumps discontinuously at rank 11 to a group of axes with close to 2/3 coincidence fraction, suggesting that the local environment of the PB's is correct for a PB/HBS tiling. Inspection of representative configurations confirms that the projected PB axes formed a PB/HBS tiling in each case. Finally, for most PB axes, with few exceptions, one centering position ($+/-$) reproduced the positions of the pole Co atoms significantly better than the other, showing that puckering patterns are also well defined.

The agreement between observed Co positions and those for a perfect PB/HBS tiling is not always exact, as shown by the less than perfect coincidences in Figure 7. Still, for the 3/4 approximant, an average of 97% of the Co atom positions agreed exactly with those of the corresponding perfect PB/HBS tiling. Similar agreement is found for the other approximants studied. We conclude that under pair potentials the PB/HBS tiling model, with the PB puckering Ising variable, is valid for small approximants.

In both the 2/3 and 3/2 approximants there is only one possible HBS tiling consistent with the lattice constants, namely the tilings consisting of hexagons only shown in Figure 4. The simulation easily finds (and remains "locked" on) these tilings, which are the experimentally observed ones. For the 3/4 approximant, there are 5 symmetry-independent HBS tilings (see Figure 6). Four of these (B,C,D,E) have mirror or glide planes consistent with full orthorhombic symmetry, while tiling A has only monoclinic symmetry. Three of the five distinct tilings of Fig. 6 (B,C,D) were observed in our simulation. With the atomic surface oversizing parameter ϵ that we chose, we lack proper sites to place a complete PB on each vertex of tiling E and did not observe this tiling in our simulation. We suspect that tiling A would appear in a sufficiently long simulation.

A representative atomic structure corresponding to tiling B is shown in Fig. 8. The dashed lines in Fig. 8 indicate the tiling change needed to transform the tiling of type B into type C. The dashed lines in Figure 8(b) form boundaries of bowtie-shaped regions, thus this flip is called a "bowtie flip" (Steurer et al. 1993, Widom and Cockayne 1995). Each tiling of Figure 6 (and its mirror images) can be reached from the others via a series of bowtie flips.

By inspection of Figure 8, we find a simple description of the atomic motion involved in the bowtie flip. It involves the exchange of an Al-Co pair separated by 2.47 Å in each puckered layer, the exchange of a Co atom with a vacancy or Al 5.5 Å away in each flat layer, along with some additional small Al atom phason hops. Details of the flat layer exchange and Al atom phason hops depend on the local Al configuration.

Individual structures in our 1000K simulations are not fully stable under relaxation using our pair potentials. We believe this reflects two deficiencies in our modeling effort. First, the ideal sites do not exactly match known positions in small approximants. The atomic surfaces should not be perfectly flat. The median displacement under relaxation of 0.2 Å is fairly consistent with the median 0.12 Å deviations of our model from experiment discussed in Section 2. Secondly, the pair potentials only approximate the total energy, which should include three- and higher-body interactions. While we believe this has only a small impact on our calculated total energies and the resulting simulated equilibrium ensemble, it can have a considerable impact on relaxation to lowest energy configurations. There are many nearly degenerate structures differing only by small atomic displacements. Any barrier between such configurations would be small. The lack of many-body interactions then could mean the difference between existence or absence of a barrier in our calculated energy landscape.

Where barriers are missing, large displacements may result even though energy changes are small.

Interestingly, in the orthorhombic Al_3Co structure (Grin et al. 1994), the largest Debye-Waller factors are reported for those sites in the Al (7 & 26) family near the edges of flat layer pentagons, and their averaged counterparts. These are the atoms that appear most mobile in our simulation. We speculate that the large Debye Waller factors confirm the very flat energy landscape described above, and these atoms will easily displace under relaxation. A minority (about 2%) of the atoms exhibit relaxations over 1 Å. Most of these large displacements are the central PB Al atom "off-centering". Whether this is an artifact of the pair potentials or represents an actual displacive transition that takes place at low temperature is an open question.

Since the experimental evidence suggests that most atoms do indeed sit near our ideal sites, we believe that our discretization of space partially compensates for our lack of many-body interactions. We believe our simulated configurations are closer to experiment than would be possible in the continuum.

PB equators occupied by just one central Al are easily distinguished from PB junction layers occupied by up to five Al. The decoration of these flat layers is strongly correlated with the vertical displacement of the Co atoms in adjoining layers. During the simulation the flat layer Al decoration fluctuates in tandem with the "puckering" discussed in the Introduction. There is greater variability in the flat layer Al configuration than may be accounted for by the puckering fluctuations alone. The PB junction layers, especially, do not exhibit a unique Al pattern. The Al concentration is sufficiently low that plenty of energetically reasonable atomic sites remain empty. Many more sites remain that cannot be occupied due to overlap with a nearby Al, but can become occupied once the nearby Al moves elsewhere. As the simulation progresses, a vast number of distinct Al configurations are visited that are all compatible with a given PB tiling and puckering pattern.

Table II gives the simulation average electron count per unit cell due to each atomic surface type, based on results for the 3/4 approximant at 1000K. The "dominant" atomic surfaces (based on average electron count times multiplicity) for the flat layers are, in order, the $\nu = 0$ atomic surface associated with the network of Co pentagons, the $\nu = 2, 3$ atomic surfaces associated with the PB junction layer Al atoms, the "averaged" atomic surfaces associated with Al atoms on the edge of a Co pentagon, and the $\nu = 1, 4$ atomic surfaces associated with the PB center Al atoms. The dominant atomic surfaces for the puckered layers are the $\nu = 1, 4$ atomic surfaces containing all the PB cap atoms and the "averaged" atomic surfaces for unpuckered atoms near the centers of the tiles. It is interesting to note that the puckered layer level 0, 2 and 3 atomic surfaces had strictly zero occupancy in the simulations. This implies that there is little tendency for reconstruction in this approximant.

The *average* structure obtained can be conveniently displayed as atomic surface maps. Figure 9 shows maps of mean Al, Co and total occupancy of each integer coordinate atomic surface that is occupied during the 1000K 3/4 simulation. The discreteness of the maps is due to the finite approximate size. The pseudo-pentagonal symmetry of the individual atomic surfaces is clear, particularly for the $\nu = 1$ and 4 puckered layer atomic surfaces. The flat layer atomic surfaces at $\nu = 0$, and puckered layer atomic surfaces at $\nu = 1$ and 4 consist of cores that are primarily Co, and Al on the outsides, while the other atomic surfaces are nearly entirely occupied by Al. The occupancy probability of the flat layer $\nu = 2$ and 3 atomic surfaces fall off rather smoothly near the atomic surface edges. Partial occupancy is the crudest characterization of disorder. We have also investigated pair correlation functions, defined by subtracting the product of two individual site occupancies from the probability of simultaneous occupation of those two sites. The strongest correlations found are negative correlations between sites separated by less than 2 Å and are due to the short-range interatomic repulsion.

Partial aluminum occupancy corresponds mainly to variability in the junction layer decoration described above. Coordinated phason fluctuations that rearrange the HBS tiling, in contrast, require both aluminum movements and aluminum/cobalt exchange. This causes the partial Al occupancy near the edges of the puckered layer atomic surfaces, as well as a thin zone of mixed aluminum/cobalt occupancy separating the cobalt and aluminum zones in the mixed atomic surfaces. In physical space, a Co-Al pair separated by 2.47 Å exchanges in each puckered layer, while a Co atom in the junction layer exchanges with an Al or vacancy 5.5 Å away (see dashed lines in Figure 8).

Finally, we discuss the disorder in the Co atom positions. On average, 3% of Co atoms are not on ideal PB/HBS tiling positions at T=1000K. We systematically investigated these defects and found that nearly all of them (95%) involve the type of Co motion associated with a phason flip (2.47 Å horizontal in puckered layer or 5.5 Å horizontal in flat layer) or a puckering flip (0.52 Å vertical motion of pole atom). These defects create stacking disorder because they occur in some, but not all, atomic layers. About a third of such defects displace Co atoms to a new position that is incompatible with a PB tiling; however these defects were always isolated, while the Co defects compatible with the bowtie flip mentioned above often occur in a coordinated way in several layers to change the tiling. Incidentally, in the high-temperature 4 Å $Al_{11}Co_4$ phase, the Al and Co positions are interchanged with respect to the PB cap decoration, *i.e.* the 2.47 Å horizontal Al-Co exchange actually becomes favored in free energy.

That observation reveals the chemical nature of phason hops in this system, and in chemically ordered systems in general. Exchanges used in are simulation are long-range with unphysical dynamics, but correct equilibrium properties. We conclude that the energy difference between a perfect PB/HBS tiling and one with bowtie flips in some layers is much less than the energy barrier associated with the Co atom being in an intermediate position (which was not observed in the sampled configurations). Chemical ordering is a problem for phason dynamics, because the short (< 2 Å) atomic phason hops in realistic atomic models destroys the chemical ordering. Preserving chemical order in the PB/HBS tiling model requires Co motion greater than 2 Å. Our simulations suggest a hierarchy of phason motion; short (< 2 Å) mainly Al atomic phason hops, and correlated phason flips that transport Co atoms more than 2 Å to their positions in another chemically ordered structure. The Co atoms spend a statistically insignificant time at intermediate positions.

Examination of the physically plausible local swaps and hops suggests that mobility of Co atoms increases greatly when some nearby Al sites are vacant. Our observations on Co hopping are consistent with the kinds of vacancy assisted hopping and diffusion discussed in Coddens et al. (1993) and Zumkley et al. (1996).

B. Energetics

We examine energetics of single atom displacements and multi-atom "flips" associated with distinct tilings and distinct patterns of puckering. At temperatures of 1000K we observe fast fluctuations of certain Al sites in addition to slow evolution of the Co positions. To investigate the nature of the excitations in more detail, we first cooled the 3/4 approximant to absolute zero temperature via simulated annealing, then we ran the Monte Carlo simulation discussed in Section III, still at absolute zero. Our annealed configuration is metastable because no hops or swaps are successful at 0K. Energy increases of the *attempted* motions are the energies of the low-lying one- and two-atom excitations. Figure 10 shows the frequency of attempted processes as a function of energy change for those Al hops, Co hops and Al-Co swaps of less than 2.5 Å and $\Delta E < 2eV$ which are most likely to be physical. The corresponding hops or swaps are identified in Table III.

Two spectral features worth noting: (1) The spectra for Al and Co hops contain sharp peaks at low energies, and show no overall increase between 0 eV and 2 eV. The spectrum for Al-Co swaps, on the other hand, rises as a broad continuum as the energy increases. (2) There are many more distinct low energy Al hops than low energy Co hops. The only low energy Co hops observed that contain a phason component are 2.34 Å and 2.47 Å hops to nearby empty sites. Interestingly, both of these hops involve the kind of junction layer site marked by an X in Figure 2(c). In fact, during the simulated annealing, 3 out of 128 Co atoms moved off puckered layer PB pole positions via 2.34 Å hops to these vacant junction layer sites. The lowest energy Co phason excitations simply move those Co atoms back to the PB poles. Curiously, there are more Co atoms on ideal PB positions on average at

1000K than at 0K. The slower rate for Co motion may be due to the need for Al vacancy assistance, rather than the relatively strong binding of Co compared with Al.

It would be useful to establish an effective free energy for different tilings and puckering patterns, in which the Co atoms are frozen in the PB/HBS tiling positions and the fast Al fluctuations are "integrated out". Formally, the full partition function can be written

$$Z = \sum_{\{\text{Co positions}\}} \sum_{\{\text{Al positions}\}} e^{-E/k_BT} = \sum_{\{\text{Co positions}\}} e^{-F_{eff}/k_BT} \tag{4.1}$$

and the effective free energy may be decomposed into

$$F_{eff} = U_{eff} - TS_{eff}. \tag{4.2}$$

Determination of F_{eff} would replace the complex problem of atomic-level thermodynamics with a simpler tiling model thermodynamics containing terms for individual tile energies and entropies as a function of temperature and corrections for the energetic and entropic interactions between tiles.

The inner sum in equation (4.1) can be evaluated, up to an overall constant factor, by simulating the Al motion while holding the Co atoms fixed. The energetic component U_{eff} is the average of the instantaneous total energies. The entropy S_{eff} may not be so easily evaluated. For the present we consider the partial information provided by the energy alone. We investigated the dependence of U_{eff} on the PB tiling and puckering pattern. Our results show small, but measurable, effects of tiling and puckering patterns on energy. The energy differences among tilings with the same numbers of hexagons, boats and stars are typically in the range of 0.001 eV/atom. There is a larger energy change, about 0.002 eV/atom, for replacing a pair of boats with a star and a hexagon. Quantitative data for some of the structures simulated is presented in Table IV.

During a run the internal energy constantly fluctuates. From the calculated heat capacity (about 0.3k$_B$/atom) at T=1000K, with 508 atoms we find RMS deviations of total energy of 1.1 eV, or 0.002 eV/atom. This energy scale for single atom fluctuations is slightly larger than the energy differences between distinct tilings. That explains why the system evolves among distinct tilings during the simulation. It also means the effective energy U_{eff} is sensitive to each atomic position, and therefore sensitive to the presence or absence of individual sites in our ideal site list. The details of the site list may dominate differences in effective energies between configurations, with the true energy differences between tilings being immeasurably small by our method.

We attempted to describe the puckering energetics in terms of the Ising spin model described in the Introduction. For each PB (labeled i) we define the Ising spin s_i. The effective energy is a function of the tiling and the spin configuration because these, together, define the Co positions. Since the puckering patterns of experimental Al_3Co and $Al_{13}Co_4$ are neither "ferromagnetic" nor "antiferromagnetic" (see Fig. 4), we include second nearest neighbor terms. It is plausible that first and second neighbor terms dominate the puckering energetics because in these cases two PB's share atoms. In the hope that the Ising variables decouple from the tiling we write the effective Hamiltonian

$$U_{eff} = U_{eff}(\text{tiling}) + \sum_{nn} J s_i s_j + \sum_{2nn} K s_i s_j. \tag{4.3}$$

To determine the magnitudes of J and K, we produced a series of different puckering configurations for the tilings. For each basic tiling, we chose fully antiferromagnetic and ferromagnetic puckering patterns (see Table IV) to give the greatest possible range in J at fixed positive K, other patterns that maximize the negative contribution of K, and random patterns. The average internal energy differences among patterns are typically of order $\approx 10^{-4}$eV/atom, implying values of J and K of order 10^{-5}eV/atom. These energy differences are small compared with energy fluctuations for single atom displacements.

If the two-coupling model of equation (4.3) were a good approximation, then the internal energies of all puckering patterns investigated for each tiling could be fit with little error. Unfortunately, it is not a good approximation, as the root-mean square error of the two-coupling model fit is 5×10^{-4} eV/atom, which is the same order of magnitude as the differences in energy of the puckering patterns being fit. We believe this failure reflects both a true failure of such a simple model and a systematic difficulty with our approach.

To illustrate the first point, consider the junction layers, and let all of the junction layer Al atoms either form distorted pentagons as shown in Figure 2 or sit on subsets of this pentagon. A full description of a configuration must specify the orientation of this distorted pentagon, *i.e.* the direction of the junction layer arrow shown in Figure 2. Preferred orientations are coupled with the Ising puckering variable and the local tiling. Even if an accurate tiling Hamiltonian with short-range pairwise interactions exists for the combination of puckering and arrow variables, averaging over arrow orientations as in equation (4.1) will likely generate long-range and multi-spin effective Ising interactions. We conclude that longer-range and/or many-cluster effects are important for stabiling certain puckering patterns in Al_3Co. In our approach, the issue is further complicated because we did not base our site list on considerations of junction layer pentagon orientation and do not even have the necessary sites to allow all orientations for each junction layer.

V. CONCLUSION

We reach several conclusions as a result of our study. This section summarizes real and perpendicular space descriptions of 8 Å AlCo structure and fluctuations, along with a description of possible improvements and directions for future work.

Our simulations reveal strong preference for spatial arrangements of atoms that fill space with pentagonal bipyramid clusters. These arrangements place clusters at vertices of some HBS tiling with edge length 6.5 Å. We have previously shown that the oscillating form of the pair potentials favors PB clusters because pair potential minima match important characteristic distances within each PB and linking neighboring PB's (Widom and Cockayne 1996). At a simulation temperature of 1000K, there is some disorder in Co atom location, but each Co pattern observed in a simulation on a 24 Å by 20 Å by 16 Å approximant can be associated uniquely with a HBS tiling. To each tiling there is associated a "puckering pattern" according to which flat layer each cluster is centered on. Different tilings occur during the 1000K simulation, as well as different puckering patterns for each individual tiling. While the puckered layer Al positions are generally well defined, many different Al arrangements are observed in the flat layers at 1000K. Puckering disorder at the temperature where the quasicrystal is metastable is likely to lead to an average structure with 4 Å periodicity and P10/mmm symmetry.

We have determined the Co positions and the aluminum occupancies in the hexagon, boat and star tiles in our approximants. The hexagon, boat and star tiles are sufficient for generating quasiperiodic structures and a simple extension of our results leads to atomic models for such quasicrystals. The bowtie phason flips that change the tiling in our simulations on approximants should also occur in the quasicrystal.

Atomic sites in our model quasicrystal are intersections of atomic surfaces with physical space. To model all of the sites in the observed Al_3Co approximants requires a few small atomic surfaces whose five-dimensional coordinates include half integers as well as several large atomic surfaces associated with integer coordinates, as listed in Table II. Because we choose over-sized atomic surfaces, we do not need to know or presuppose detailed atomic surface shapes. Indeed, we find that a statistical description of atomic surfaces is necessary at a temperature of 1000K. When both Al and Co share an atomic surface, the Co occupies the middle, while the Al forms a shell around it. There is a smooth fall-off of occupation probability near the boundaries of the surfaces and a smooth transition of occupation probability from Co to Al. Both these smooth transitions reflect distinct forms of phason disorder.

Our simulation visits an entire family of probable configurations. This includes both ideal cluster packings and characteristic low energy fluctuations that transform one ideal structure into another. By far the most common type of fluctuation are movement of those aluminum atoms near the atomic surface edges. The Co positions change with much lower frequency. We believe the Co mobility is highly dependent on the presence of Al vacancies. From the attempted hop energy spectra in Figure 10 we note that many possible hops require less than 5 $k_B T$ (=0.43 eV at T=1000K) energy, implying a reasonable chance for acceptance. Indeed, there is no effective lower bound on the attempted hop energy. Our simulation continues to display Al vacancy hopping at room temperature (T=300K) and below. Because these atoms occupy sites near the atomic surface edges, the vacancy hopping is a type of phason fluctuation.

Al motion and Al-Co swaps contribute to two kinds of collective fluctuations in our simulations that preserve the PB/HBS description. One of these (the "puckering flip") shifts a column of clusters 4 Å along its axis; the other (the "phason flip") moves a column of clusters 2.5 Å in a direction perpendicular to its axis and rotates it 180 degrees. In each flip, most atoms remain stationary or move very small distances. Puckering flips occur with greater frequency than phason flips. Our observation of puckering reversals within a given tiling, and phason flips between tilings, implies that the energy cost of such fluctuations is low enough that they occur readily in equilibrium at T=1000K.

We now summarize possible inadequacies of our methods and results. The ideal sites do not capture the observed Al and Co positions exactly. While the median distance of experimental sites from ideal is 0.12 Å, a few sites lie as much as 0.58 Å away. Furthermore, a small number of atoms exhibit large displacements under relaxation. We believe that present Al-TM pair potentials are inadequate to treat relaxation properly.

The comparative energetics of differing tilings and puckering patterns are very sensitive to the inclusion or exclusion of certain sites, in particular the special sites in the flat and puckered layers. To make matters worse, our site list constructed according to the discussions of Section 2 does not yield full local 5-fold rotational symmetry within PB clusters, introducing the systematic error discussed in the previous section. To investigate sensitivity to the site list, we added carefully chosen sites to the site list, especially those that maximize local pentagonal symmetry on possible cluster axes. Simulations confirmed that the energy depends on inclusion of particular sites at a level comparable to the energy differences between distinct tilings. Our results for the energy differences between tilings must thus be taken as upper estimates only.

We have not found a temperature-dependent effective tiling Hamiltonian. Such a Hamiltonian, once obtained, would allow simulation studies of the fundamental and interesting question of the nature of the stability of the quasicrystalline phase. Further progress requires both a new method for site list construction that respects local symmetry, and inclusion of long-ranged and many-body couplings in the effective Hamiltonian.

Finally, we compare this work with similar efforts. Mihalkovič *et al.* (1996a, 1996b) used pair potentials to find tile energies and interaction energies of tiles for a canonical cell model of icosahedral AlMn at zero temperature and succeeded in creating a "zero temperature" tiling Hamiltonian. We focused, on the other hand, on finite temperature structures and found a large source of entropy due to Al rearrangements within the tiles that we were unable to quantify. Based on the large number of Al sites with partial occupancy, and the small number of different tilings, the internal Al disorder entropy is likely to be larger than the tiling entropy at 1000K (for a tiling description at the 6.5 Å length scale). We conjecture that this is true for complex Al-TM phases in general.

Dmitrienko and Astraf'ev (1995) combined energetics with a growth model to define a set of ideal sites. That is, their site list evolved as the quasicrystalline structure grew. An approach of this type might help solve our problem of systematic errors in U_{eff} arising from the site list construction. The idea would be to replace the site list with atomic surface occupancy directly in the higher dimensional space. The equivalent of our discretization of space would be placing a limit on perpendicular space deviations between neighboring atoms. The fall-off in atomic surface occupancy near the edges suggests such a cut-off may easily be implemented.

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FIGURES

FIG. 1. (a) Two-level hexagon-boat-star (HBS) tiling formed by removing a subset of vertices from the Penrose rhombus tiling. (b) Random HBS tiling.

FIG. 2. (a) Pentagonal bipyramid cluster containing 16 aluminum and 7 cobalt atoms. (b) Exploded view showing equator and caps. In both simulated and observed structures, some equator Al atoms are displaced to the midpoints of their Co neighbors. (c) Flat layer junction. All Al sites have partial occupancy. The sites marked by an X also have partial Co occupancy. The long axis of the distorted pentagon defines an orientation, indicated by the arrow.

FIG. 3. Experimental and ideal atomic sites for the 2/3 approximant. (a) Flat layer F. (b) Puckered layer P. Clockwise from lower left: ideal and averaged sites labeled with atomic surface number; experimental structure (atoms labeled as in the structure refinement of Grin *et al.* (1994)); ideal and experimental superimposed; same with averaged sites added.

FIG. 4. Tiling and puckering patterns observed in (a) monoclinic $Al_{13}Co_4$ and (b) orthorhombic Al_3Co. The pseudo-centered-orthorhombic supercell of the monoclinic phase is highlighted.

FIG. 5. Possible reconstruction of two hexagons and a boat of edge length 6.5 Å into a symmetric decagon of diameter 20 Å.

FIG. 6. All symmetry-independent hexagon-boat-star tilings allowed for the 3/4 orthorhombic cell.

FIG. 7. Average coincidence fraction f between Co positions for N'th best cluster axis in a T = 1000 K Al-Co simulation and the Co positions for perfect pentagonal bipyramid (PB) cluster centered on this axis. The horizontal line at $f = 2/3$ represents the maximum coincidence for an axis external to a given PB in a PB/HBS tiling. Note the clear division between PB axes for $N \leq 10$ and non-PB axes for $N > 10$ as expected in the hexagon-boat-star tiling model.

FIG. 8. Atomic positions in (a) flat layer and (b) puckered layer for a representative 1000 K simulation configuration. A 2 by 2 supercell of the simulation cell is shown. Open circles denote aluminum atoms, while filled circles denote cobalt atoms. This configuration represents tiling B of Figure 6. The dashed lines indicate the single bowtie phason flip per unit cell needed to convert this tiling into a tiling of type C.

FIG. 9. Maps of the atomic surfaces obtained by simulating a AlCo 3/4 orthorhombic approximant at $T = 1000K$.

FIG. 10. "Energy spectra" for (top) short Al hops, (middle) short Co hops and (bottom) short Al/Co swaps.

TABLES

TABLE I. List of important distances in our model. For AlCo, we use quasilattice parameter $a_0 = 1.529$ Å, periodicity along decagonal axis $c = 8.120$ Å, and puckering parameter $p = 0.260$ Å.

Total distance (Å)	In-plane distance	Vertical distance	Total distance (Å)	In-plane distance	Vertical distance
0.260	0	p	2.353	$\tau \cos(\pi/10)\, \mathrm{a}_0$	0
0.520	0	$2p$	2.474	$\tau\, a_0$	0
0.539	$\tau^{-1} a_0/2$	p	2.908	$2 \cos(\pi/10)\, \mathrm{a}_0$	0
0.765	$a_0/2$	0	4.706	$2\,\tau \cos(\pi/10)\, \mathrm{a}_0$	0
0.945	$\tau^{-1} a_0$	0	5.532	$\sqrt{5}\,\tau\, a_0$	0
1.529	a_0	0	6.477	$\tau^3\, a_0$	0
2.290	0	$c/4 + p$	7.614	$2\,\tau^2 \cos(\pi/10)\, \mathrm{a}_0$	0
2.339	a_0	$c/4 - p$	8.120	0	c

TABLE II. Atomic surfaces included. We used $\epsilon = \tau^{-3}/2 \approx 0.118$ in this study. The remaining atomic surfaces differ only in their z coordinate and generated by z+0.5 and −z. The average electron count in individual atomic surfaces is given as determined by simulation, showing the absence of certain atomic surfaces.

z	Level(s)	Multiplicity	Radius (units of $a_\perp$)	Ave. electron count (simulated)
0.25	0	2	$1+\epsilon$	702
0.25	2,3	4	$1+\epsilon$	140
0.25	1,4	4	$\tau^{-2}+\epsilon$	27
0.25	(averaged)	10	(see text)	18
0.282	0	4	$\tau^{-3}+\epsilon$	13
0.468	1,4	8	$1+\epsilon$	227
0.468	2,3	8	$\tau^{-2}+\epsilon$	0
0.5	0	2	$\tau^{-3}+\epsilon$	0
0.5	(averaged)	10	(see text)	21

TABLE III. Prominent low-energy peaks in excitation spectra (Figure 10 (a) and (b)) and associated atomic motion

Energy(eV)	move type
0.04	Al 0.765 Å
0.10	Co 2.339 Å
0.12	Al 0.520; 0.539 Å
0.15	Co 2.339 Å
0.20	Co 0.520 Å
0.21	Al 0.539 Å
0.28	Co 0.260 Å
0.29	Al 0.520 Å
0.45	Co 0.260 Å
0.51	Al 0.520; 0.945 Å

TABLE IV. Selected results for simulations with fixed Co patterns. Data based on three runs of 150000 attempted Monte Carlo steps per atom for each tiling and spin configuration. The form of a two interaction tiling Hamiltonian for U_{eff} is also shown.

Type	U_{eff}	Energy (eV/atom)	Specific heat (k_B)
B antiferro	U_B-14J+10K	0.11337(7)	0.280(9)
B ferro	U_B+14J+10K	0.11275(5)	0.275(7)
C antiferro	U_C-14J+10K	0.11385(6)	0.299(7)
C ferro	U_C+14J+10K	0.11331(4)	0.293(5)
D antiferro	U_D-14J+11K	0.11602(4)	0.285(8)
D ferro	U_D+14J+11K	0.11467(7)	0.288(6)